

WHAT IS CLAIMED IS:

5 1. A method for determining the presence and concentration of gases by means of monitoring the change in photons in a sensing system comprising passing photons through a waveguide, which is coated with a porous transparent material and impregnated with a sensing media: and further comprising a means to couple the optical signal in the waveguide to the sensing material in the coating via evanescent wave absorption, and further comprising a display means, and further comprising at least one sensor which response to at least one target gas and can be monitored by an electronic circuit and further comprising a photon emitter and a photon detector.

15 2. A method as claimed in claim 1 further comprising at least one optically responding sensor(s), which is monitored by a photon source and photodetector and is calibrated to initiate a signal at a predetermined level of target gas for a predetermined period of time, the method comprising the steps of:

20 intermittently measuring the optical (transmission) characteristics of the sensor(s); and calculating the amount of target gas present.

25 3. A claim as in claimed 1 further comprising a means of differential measurement from a control sensor not exposed to the target gas, and further comprising a control sensor that responds to the environment the same as the target gas sensor with the same optical characteristic changes over time temperature, humidity, smog, and other conditions as the gas sensor; and further a means to prevent the target gas from reacting to the control sensor.

30 4. A claim as in claim 1 where the target gas is carbon monoxide.

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5 5. An apparatus that measure the identity and concentration of gases and vapors comprising at least one optical evanescent field absorption sensor; and further comprising a photon emitter and photon detector; and further comprising a waveguide coated with a porous transparent material.

10 6. An apparatus as claimed in claim 5 comprising a porous transparent material that is an oxide; and further comprising a sensing material coated onto the transparent porous oxide that changes its optical properties when exposed to a target gas.

15 7. An apparatus as claimed in claim 5 comprising a set of EFA sensors that respond to a variety of target gases and the identity of the target gas is determined by the wavelengths and intensity of the absorption.

20 8. An apparatus as claimed in claim 6 comprising a ring waveguide coated with a sensing material; and further comprising a straight waveguide section and a means to couple photons from the straight waveguide to the ring waveguide and remove a portion of those photons and then detect a target gas by monitoring the amount of photons at the end of the straight waveguide.

25 9. An apparatus as claimed in claim 6 where the target gas is carbon monoxide.

30 10. An apparatus as in claim 9 wherein the sensing material is a chemical reagent comprising at least one of the following groups:

Group 1 Palladium salts selected from the group consisting of palladium sulfate, chloride, bromide.

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Group 2 Heteropolymolybdates such as silicomolybdic acid,
ammonium

5 molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and
perchlorate.

Group 4 Alpha. beta gamma or delta cyclodextrins and there
hydroymethy ethyl and propyl derivatives.

10 Group 5 Soluble salts of alkaline and alkali chlorides and
bromides and mixture thereof;

Group 6 Organic solvent and/or co-solvent and trifluorinated
organic anion selected from the group including dimethyl sulfoxide
(DMSO), tetrahydrofuran (THF), dimethyl formamide (DMF),
15 trichloroacetic acid, trifluoroacetate, a soluble metal
trifluoroacetylacetonate selected from cation consisting of copper,
calcium, magnesium, sodium, potassium, lithium, or mixture thereof;
and

20 Group 7 Soluble inorganic acids such as hydrochloric acid,
sulfuric acid, sulfurous acid, nitric acid, and strong oxidizers
such as peroxide, or mixture thereof.

11. A method as claimed in claim 1 comprising the process of
fabricating the EFA sensing device comprising the steps of coating
25 the waveguide with a porous silica layer between 20 nm and 200 nm
and then coating the porous silica surface with a sensing agent.

12. The method as claimed in claim 11 wherein the step of
coating the waveguide is to immerse the waveguide in a chemical
30 reagent comprising at least one of the following groups for several
hours:

Group 1 Palladium salts selected from the group consisting of
palladium sulfate, chloride, bromide and mixture thereof;

35 Group 2 Heteropolymolybdates such as silicomolybdic acid,
ammonium molybdate, alkali metal molybdates

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Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

5 Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

10 Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s); and

15 Group 7 Strong oxidizer such as nitric acid, hydrogen peroxide or mixture thereof and further removing the waveguide and porous outer layer from the solution and then dry the waveguide system slowly over 1 to 2 days to form the supramolecular sensing complex.

20 13. A method of producing the porous transparent layer which provide the sensing platform for a sensing agent in evanescent filed absorption sensor is made by starting with a silicon alkoxide; and further comprising the step of reaction the silicon alkoxide with a organic material with carbons from 4 to 12; and further in voles hydrolysis of the complex to for an Organo-silicon compound that is stable a soluble in non-polar solvents and further dissolving the solid Organo-silicon in the solvent and then coating the waveguide
25 with the solution and further drying the coating and then heating it to drive off the solvent.

30 14. The method of claim 13 further comprising the steps of adding a pore forming agent to the solvent containing the organo-silicon; and then coating the waveguide, drying and heating to remove all solvent and to burn out the pore forming agent that results in a 150 to 300 nm pore structure.

35 15. The method of claim 14 wherein the pore agent is a soluble polymer of more than 100 carbons.

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16. A method of measuring the concentration of carbon
monoxide using a porous transparent monolith that is coated with a
5 chemical sensing agent comprising an optical cavity that surrounds
the sensor on at least 2 reflective surface facing each other with
the sensor in between them and there is further a photon source that
emits photons that are pass through the sensor monolith and are then
striker the reflector; and further the photons are reflected of the
10 surface and direct to pass through the sensor again and this process
repeat at least one more cycle striking the second reflector and
being direct to pass through the transparent sensor place between
the reflectors that response with an optical change proportional to
the CO exposure ands the speed of detection proportional to the
15 number of times the photon beam passes though the sensor before
striking the photon detector.

17. A method as claimed in claim 16 that comprises a silica
porous monolith with average pore diameter of 10 to 30 nm and the
20 sensing agent is applied by immerse the porous transparent silica
monolith in a chemical reagent comprising at least one of the
following groups for several hours:

Group 1 Palladium salts selected from the group consisting of
palladium sulfate, chloride, bromide and mixture thereof;

25 Group 2 Heteropolymolybdates such as silicomolybdic acid,
ammonium molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and
mixtures thereof,

30 Group 4 Alpha, beta, gamma, and or delta cyclodextrins and
their derivatives and mixtures thereof,

Group 5 Soluble salts of alkaline and alkali chlorides and
bromides and mixture thereof;

35 Group 6 Inorganic or organic acid and or salt of organic or
inorganic compound that dissolve in the mixture in the presence of
the acid(s); and

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Group 7 strong oxidizer such as hydrogen peroxide and or
nitric acid. and further removing the waveguide and porous outer
5 layer from the solution and then dry the waveguide system slowly
over 1 to 2 days to form the supramolecular sensing complex.

18. A method as claimed in claim 17 where the porous silica
is made by a solgei method and the average pore diameter id 16 nm to
10 27 nm.

19. A method as claimed in claim 14 comprising a process for
monitoring the response of a set of EFA sensors; and further
comprising a means to determine the value of one or more target gas
15 concentrations in a fashion so as to rapidly determine the danger
levels, TWA, total dose, and peak concentration over a pre-selected
period.

20. An apparatus as claimed in claim 10 where the device
20 comprises a microprocessor and where there is are several photon
sources of different
wavelengths and at least one photon detector and there is a means to
measure each wavelength separately by pulsing the photon source at
different time and reading the many different wavelengths; and
25 further an analog to digital converter to convert the analog signal
to digital and further comprise a means to store the digitized
signal from each wavelength and compare the signal patterns form
each wavelength to a pattern stored in the microprocessor and an
algorithm that will interpret the various signal patterns to
30 identify the gases present and estimate their concentrations.

21. An apparatus as claimed in claim 5 comprising a waveguide
in the shape of a ring and further comprising a very thin coating on
the ring with a sensing material in the coating; and further
35 comprising a straight waveguide in the immediate vicinity and

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running tangent to the ring waveguide and a means to switch the photons from the straight waveguide to the ring waveguide and a means to switch the photon from the ring back to the straight waveguide and a means to detect the change in evanescent field absorption due to one or more target gases by monitoring the amount of photons at the end of the straight waveguide.

10 22. An apparatus as claimed in claim 21 comprising more than one light source each with different wavelengths and a means to read each wavelength independently.

23. An apparatus as claimed in claim 22 further comprising several photon sources of different wavelengths and at least one photon detector and there is a means to measure each wavelength separately by pulsing the photon source at different time and reading the many different wavelengths; and further an analog to digital converter to convert the analog signal to digital and further comprise a means to store the digitized signal from each wavelength and compare the signal patterns from each wavelength to a pattern stored in the microprocessor and an algorithm that will interpret the various signal patterns to identify the gases present and estimate their concentrations.

25 24. A multi-pass photon sensing gas detector apparatus for determining the target gas concentration and identity comprises: a microprocessor and a means for assigning sensor reading values to each of the measured optical characteristics; means for determining differences between sensor reading values;

30 memory for storing the differences; an alarm register for adding the sum of a plurality of the differences stored in the memory; and means for entering an alarm mode when value of the alarm register exceeds an alarm point; and further comprising a sensing system as follows: a porous transparent monolith "that is coated with a chemical sensing agent comprising an optical cavity that surrounds the sensor

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on at least 2 reflective surface facing each other with the sensor in between them and there is further a photon source that emits photons
5 that are pass through the sensor monolith and are then striker the reflector; and further the photons are reflected of the surface and direct to pass through the sensor again and this process repeat at least one more cycle striking the second reflector and being direct to pass through the transparent sensor place between the reflectors that
10 response with an optical change proportional to the CO exposure ands the speed of detection proportional to the number of times the photon beam passes though the sensor before striking the photon detector.

25. A multi-pass photon gas detection apparatus as claimed in
15 24 comprising a means to optically sense at least two sensors in a differential measuring system comprising:

an optical means to sense the target gas; a control optical means for sensing the environment the same as the target gas sensor but does not respond to the gas;

20 measuring means for measuring the difference in the characteristics of the sensor; and control;

means for determining magnitude of the measured difference in optical characteristics and the intensity of the difference, including a means to monitor accurately the target gas concentration when first
25 sensor responding to the target gas and control sensor regenerates so fast no optical response is seen.

26. A multi-pass photon gas detection apparatus as claimed in claim 25 comprises:

30 at least one photon source; and at least one photodetector optically coupled with the sensor and the photon source for producing a photocurrent proportional to the measured characteristics of the sensor; and

further comprising a control sensor and a means to measure the
35 difference between any CO sensor and the control a capacitor coupled

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to the photodetector, the capacitor being charged by the photocurrent;
and

5 a microprocessor coupled to the capacitor for measuring time for
charge on the capacitor to reach a threshold, the measured time being
proportional to the darkness of the sensor.

10 27. A multi- pass photon gas detection apparatus as claimed in
claimed 25 comprising an A to D converted to digitize the signal from
the photodetector; and

further comprising a means to incorporate the device into a fuel
cell vehicle to control the reformer process by measuring CO in
milliseconds; and

15 further comprises a sensor to selectively detect CO in the
presence of hydrogen and CO₂; and further comprising a porous
transparent monolith that is coated with a chemical sensing agent
comprising an optical cavity that surrounds the sensor on at least 2
reflective surface facing each other with the sensor in between them
20 and

there is further a photon source that emits photons that are pass
through the sensor monolith and are then strike the reflector; and
further the photons are reflected off the surface and direct to pass
through the sensor again and this process repeat at least one more
25 cycle striking the second reflector and being direct to pass through
the transparent sensor place between the reflectors that response with
an optical change proportional to the CO exposure and the speed of
detection proportional to the number of times the photon beam passes
though the sensor before striking the photon detector.

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28. An evanescent photon absorption sensor based gas detector
apparatus as in claim 6 comprising at least 2 sensors and sensor
monitoring system and a means to condition the sample and a means to
switch the gas from the reformat stream to a air stream and back
35 periodically; and further comprising a microprocessor control the

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switching and to process and digitize the signals from the photodetector(s) to determine the CO gas concentration in a fuel cell reformate stream, and further comprising a means to incorporate the device into a fuel cell vehicle to control the reformer process by measuring CO in milliseconds; and further comprises a sensor to selectively detect CO in hydrogen and CO₂, a means indicate need of service, and a means to protect the occupants from the gases detected.

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29. An evanescent photon absorption sensor based gas detector apparatus as claimed in claim 28 further comprising:

at least two photon sources in each sensing chamber;

at least one photodetector optically coupled to receive photons from the photon sources as modified by the sensor and at least two photon source for emitting photons at different wavelengths that in term measure the response of the sensor(s) to CO and humidity; and a means to determine the CO and humidity component to the signal; and

further comprising a chemical reagent comprising at least one of the following groups for several hours:

Group 1 Palladium salts selected from the group consisting of palladium sulfate, chloride, bromide and mixture thereof;

Group 2 Heteropolymolybdates such as silicomolybdic acid, ammonium molybdate, alkali metal molybdates

Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s).

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30. An evanescent photon absorption sensor based gas detector apparatus as claimed in claim 2 comprising a means for controlling the reformer of a fuel cell where the device comprises a microprocessor and where there is are several photon sources of different wavelengths and at least one photon detector and there is a means to measure each wavelength separately by pulsing the photon source at different time and reading the many different wavelengths; and further an analog to digital converter to convert the analog signal to digital and further comprise a means to store the digitized signal from each wavelength and compare the signal patterns form each wavelength to a pattern stored in the microprocessor and an algorithm that will interpret the various signal patterns to identify the gases present and estimate their concentrations.

31. An evanescent photon absorption sensor based gas detector apparatus as claimed in claim 6 comprising two sensors in two separate housing each comprising more than one photon source each of a different wavelength; and further comprising a sample conditioning system that consist of a thermoelectric cooling section and a heating section, between the cold section and the heating section is a membrane to prevent water from passing and a means to periodically remove excess water; and further comprising

the CO detector system with at least two separate chambers with valves connecting the sensors alternately to the air and a reformat gas sample; further comprising a display means to indicate the need to perform maintenance; and further comprising at least two sensor, which one responses to the CO in the hydrogen stream while at least one remains outside the stream and is regenerated in clean air, and further comprising a means to switch the flows of clear air through one of the sensor chambers and a portion of the hydrogen stream through another sensor chamber and a control means to assure that the concentration of CO directed to the fuel cell is less than a pre- determined; and further comprising and further comprising at least two optically

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responding sensors, which response to the CO and humidity; and can be
monitored by a low-powered electronic circuit with a current draw of
5 less than 25 microamps; and further comprises a supramolecular complex
that is self assembled on to a semi-transparent silica porous
substrate; and further comprising a thin semi-transparent sensing layer
on the porous transparent substrate comprising palladium, copper and
calcium metals ions, halogen anions and cyclodextrins and there
10 derivatives and an acid.

32. A method as in claim 13 comprising a process at least one
optically responding sensor(s) monitored by two different photon
sources and a photodetector and the system is calibrated to initiate
15 a signal at a predetermined level of target gas for a predetermined
period of time, the method comprising the steps of: intermittently
measuring the optical (transmission) characteristics of the sensor(s);
and further comprising a means to monitor a reformat stream by
sampling the stream alternately as a means to alternately direct a
20 sample of gas to the first sensor and air to the second sensor and the
to reverse the process to allow the first sensor to regenerate and
further comprising a sample condition means so that sample of reformat
and air enter the sensing chambers at a predetermined relative
humidity, pressure and temperature.

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33. A device as claimed in claim 5 further comprising micron
size sensors that can modify their photon properties to signal an
indication of a gas detection, which is proportional to changes in the
way photon interact with the material.

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34. An apparatus a claimed in claim 28 further comprising a that
is use to calculate the CO concentration and further a means to display
the digital value of the CO concentration, further comprising a mean
to measure an compensate for temperature value; and further comprising
35 a sensor which consist of a porous silica materials coated with a

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chemical reagent comprising at least one of the following groups: Group
1: Palladium salts selected from the group consisting of palladium
5 salts of sulfate, palladium sulfite, palladium pyrosulfite, palladium
chloride, palladium bromide, palladium iodide, palladium perchlorate,
 CaPdCl_4 , CaPdBr_4 , Na_2PdCl_4 , Na_2PdBr_4 , K_2PdCl_4 , K_2PdBr_4 , Na_2PdBr_4 ,
 $\text{CaPdCl}_x\text{Br}_y$, $\text{K}_2\text{PdBr}_x\text{Cl}_y$, $\text{Na}_2\text{PdBr}_x\text{Cl}_y$ (where x can be 1 to 3 if y is 4 or
visa versa), and organometallic palladium compounds such as palladium
10 acetamide tetrafluoroborate and other similarly weakly bound ligands,
and mixtures of any portion or all of the above; Group 2: Molybdenum,
vanadium, and/or tungsten salts or acid salts selected from the group
consisting of silicomolybdic acid, phosphomolybdic acids, and their
soluble salts, molybdenum trioxide, ammonium molybdate, alkali metal,
15 or alkaline earth metal salts of the molybdate anions, mixed
heteropolymolybdates, or heteropolytungstenates and mixtures of any
portion or all of the above; Group 3: Soluble salts of copper halides,
sulfates, nitrates, perchlorate, and mixtures thereof, copper
organometallic compounds that regenerate the palladium such as copper
20 tetrafluoroacetic acid, copper tritlouroacetylacetonate, and other
similar copper compound, and copper vanadium compounds such as copper
vanadate, and soluble vanadium compounds that can be incorporated into
the group 2 molybdenum based-keg ions such as phosphomolybdic acid and
silicomolybdic acid, and mixtures of any portion or all of the above;
25 Group 4: Supramolecular complexing molecules selected from the
cyclodextrin family including alpha, beta, and gamma as well as their
soluble derivatives such as hydroxymethyl, hydroxyethyl, and
hydroxypropyl beta cyclodextrin, crown ethers and their derivative, and
mixtures of any portion or all of the above; Group 5: Soluble salts of
30 alkaline and alkali halides, and certain transitional metal halides
such as manganese, cadmium, cobalt, chromium, nickel, zinc, and other
soluble halide such as aluminum; and any mixture thereof; Group 6:
Organic solvent and/or co-solvent and trifluorinated organic anion
selected from the group including dimethyl sulfoxide (DMSO),
35 tetrahydrofuran (THF), dimethyl formamide (DMF), trichloroacetic acid,

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trifluoroacetate, a soluble metal trifluoroacetylacetonate selected from
cation consisting of copper, calcium, magnesium, sodium, potassium,
5 lithium, or mixture thereof; Group 7: Soluble inorganic acids such as
hydrochloric acid, sulfuric acid, sulfurous acid, nitric acid, and
strong oxidizers such as peroxide, or mixture thereof.

35. The apparatus of claim 28 wherein the microprocessor
10 comprises a means for assigning sensor reading values to each of the
measured photon characteristics; means for determining differences
between sensor reading values;

memory for storing the differences;

an alarm register for adding the sum of a plurality of the
15 differences stored in the memory; and

means for entering an alarm mode when value of the alarm register
exceeds an alarm point and a means to signal when the change has
occurred above a predetermined level.

20 36. An apparatus as claimed in 29 comprising a means to sense
at least two sensors in a differential measuring system comprising:

a photon sources and detector means to sense the target gas ; a
control means for sensing environment parameters that affect the target
gases and compensate for those changes;

25 a means for measuring the difference in the characteristics of
the sensor; and a means for determining magnitude of the measured
difference in photon characteristics and the intensity of the
difference, including a means to monitor accurately the target gas
concentration under a wide range of temperature and humidity.

30 37. A gas sensing gas detector apparatus for determining the
target gas concentration comprises: a photon source and a sensor that
changes its index of refraction when exposed to the target gas; and
further comprising

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two waveguides one located on opposite sides of the sensor; and further comprising a means to measure the intensity of photon that are
 5 switched from waveguide 1 which is illuminated by the photon source to second waveguide proportional to the concentration of target gas; and further comprising a means for entering an signal or control mode when value of photon intensity changes exceeds a predetermined level; and further comprising a sensing system comprising a porous transparent
 10 monolith that is coated with a chemical sensing agent comprising an optical element coupling the two waveguides and further

the sensor in between the two waveguides pass photons from first waveguide to the second waveguide in proportion to the amount of target gas exposed to the sensor.

15 38. A gas detection apparatus as claimed in 37 comprising a means to optically sense at least two sensors in a differential measuring system comprising:

an optical means to sense the target gas ; a control optical
 20 means for sensing the environment the same as the target gas sensor but does not respond to the gas;

measuring means for measuring the difference in the characteristics of the sensor; and control

means for determining magnitude of the measured difference in
 25 optical characteristics and the intensity of the difference, including a means to monitor accurately the target gas concentration when first sensor responding to the target gas and control sensor regenerates so fast no optical response is seen.

30 39. A gas detection apparatus as claimed in claim 37 comprises: at least one photon source; and at least one photodetector optically coupled with the sensor and the photon source for producing a photocurrent proportional to the measured characteristics of the sensor; and further comprising a control sensor and a means to measure
 35 the difference between any CO sensor and the control

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a capacitor coupled to the photodetector, the capacitor being charged by the photocurrent; and

5 a microprocessor coupled to the capacitor for measuring time for charge on the capacitor to reach a threshold, the measured time being proportional to the darkness of the sensor.

10 40. A miniaturized porous substrate less than one micron in any dimension coated with a sensing chemical that response by changes its optical transmission to carbon monoxide comprising a photon source and a photon detector; and

further comprising a microprocessor to control the photon sources and the photon detector.

15 41. A very small sensing device as claim in claimed in 40 comprising a porous transparent substrate and further comprising a chemical reagent coated onto the high surface area of the porous substrate and further comprising at least one of the following groups of compounds to form a CO sensing material:

20 Group I Palladium salts selected from the group consisting of palladium sulfate, chloride, bromide and mixture thereof;

Group 2 Heteropolymolybdates such as silicomolybdic acid, ammonium molybdate, alkali metal molybdates

25 Group 3 Copper salts of sulfate, chloride, bromide and mixtures thereof,

Group 4 Alpha, beta, gamma, and or delta cyclodextrins and their derivatives and mixtures thereof,

30 Group 5 Soluble salts of alkaline and alkali chlorides and bromides and mixture thereof;

Group 6 Inorganic or organic acid and or salt of organic or inorganic compound that dissolve in the mixture in the presence of the acid(s).

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